2.2. MASS SPECTROMETRY

Structure:

2.2.1.	Introduction
2.2.2.	Instrumentation
2.2.3.	ION Production
2.2.4.	Types of Ionization
2.2.5.	Fragmentation of Organic Compounds
2.2.6.	Meta Stable Peak
2.2.7.	Mc Lafferty Rearrangement
2.2.8.	The Nitrogen Rul
2.2.9.	Halogen Compounds
2.2.10.	Alkanes
2.2.11.	Alkenes
2.2.12.	Alkyl Aromatic Compounds
2.2.13.	Ethers
2.2.14.	Alcohols
2.2.15.	Ketones
2.46	Currented Pandings

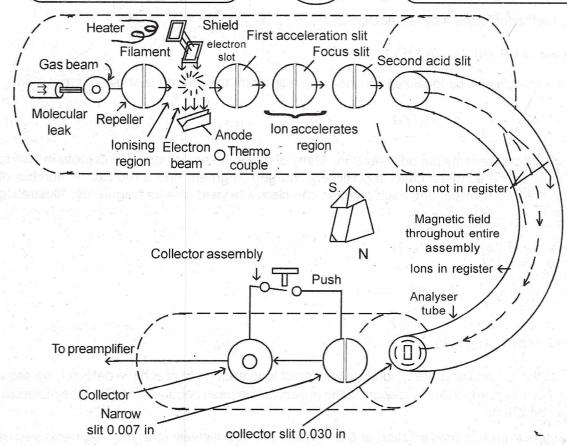
2.2. MASS SPECTROMETRY

2.2.1. Introduction:

Mass spectrometry is one of the most versatile technique used to characterize organic compounds. It is also useful method for determining the molecular mass of the compound and its elemental composition. In this technique, the molecules are bombarded with a beam of energetic electrons. The molecules are ionized and broken up into many fragments, some of which are positive ions. Each kind of ion has a particular ratio of mass to charge (i.e.) m/e ratio. In mass spectrum a signal is obtained for each value of m/e that is represented. The intensity of each signal represents the relative abundance of the ion producing the signal. The largest peak in the spectrum is called the base peak and its intensity is taken as 100. The intensities of other peaks are represented relative to the base peak.

Mass spectra is used in the following two general ways:

- i) To prove the identity of two compounds
- ii) To establish the structure of a new compound
- **2.2.2.** Instrumentation: Mass spectrometers of both low and high resolution are available. A typical 180° single focusing low resolution mass spectrometer shows the following components.
- **1. Sample Handling System :** This consists of a device for introducing the sample, a micromanometer for determining the amount of sample introduced, a device (molecular leak) for metering the sample to the ionization chamber and a pumping system. Sample sizes for liquids and solids range from several milligrams to less than a microgram, depending on the method of introduction and the detector. For routine work, vapour pressure of 10-1 to 10-3 torr is desired.
- 2. Ionization and Accelerating chambers: The gas stream from the molecular leak enters the ionization chamber in which it is bombarded at right angles by an electron beam emitted from a hot filament. Positive ions produced by interaction with the electron beam are forced though the first acceleration slit by a small electrostatic field between the repellers and the first acceleration slit. A strong electrostatic force between the first and second accelerating slits accelerates the ions to their final velocities. To obtain a spectrum, either the magnetic field applied to the analyzer tube or the accelerating voltage between the first and second ion slits is varied. Thus the ions are focussed at the collecter slit as a function of mass.
- 3. Analyzer Tube and Magnet: The analyzer tube is an evacuated, curved, metal tube through which the ion beam passes from ion source to the collector. The magnetic pole pieces are mounted perpendicular to the plane of the diagram. The main requirement is a uniform and stable magnetic field.
- **4. Ion Collector and Amplifier :** A typical ion collector consists of one or more collimating slits and a faraday cylinder; the ion beam impinges axially into the collector, and the signal is amplified by an electron multiplier.
- **5. Recorder:** A widely used recorder uses five separate galvanometers that record simultaneously. Peak heights are proportional to the number of ions of each mass.



Schematic diagram of 180° single focussing Mass spectrometer

2.2.3. ION Production:

Mass spectra are routinely obtained at an electron beam energy of 70 e.v. The simplest event that occurs is the removal of a single electron from the molecule in the gas phase by an electron of the electron beam to form a molecular ion, which is a radical cation (M⁺). The highest occupied orbital of aromatic system and non bonding electron orbitals on Oxygen and Nitrogen atoms readily lose one electron. An electron from double bond or triple bond is usually lost. In alkanes the ionization of C-C sigma bond is easier than that of C-H bonds.

$$\begin{array}{c} M \overset{+e}{\rightarrow} M^+_{(g)} + 2e \\ & & \\ & & \\ \hline \\ Benzene & Parent ion \\ \hline \\ R-O-H \overset{-e}{\rightarrow} R-O-H+2e \\ & \\ \hline \\ Parent ion \\ \end{array}$$

For ex: Methanol forms a molecular ion

$$CH_3OH + e \rightarrow CH_3OH^+$$
 (m/e 32)+2e

When the charge can be localized on one particular atom, the charge is shown on that atom.

The single dot represents the odd electron. Many of these molecular ions disintegrate in 10^{-10} to 10^{-3} Sec to give, in the simplest case, a positively charged fragment and a radical. A number of fragment ions are thus formed, and each of these can cleave to yield smaller fragments. Illustrating with methanol.

$$CH_3OH^+ \rightarrow CH_2OH^+ (m/e 31) + H$$
.

$$CH_3OH \rightarrow CH_3^+ (m/e 15) + .OH$$

$$CH_2OH^+ \rightarrow CHO^+ (m/e 29) + H_2$$

If some of the malecular (parent) ions remain intact long enough to reach the detector, we see a molecular ion peak. It is important to recognize the molecular ion peak because this gives the molecular weight of the compound.

A mass spectrum is a presentation of the masses of the positively charged fragments versus their relative concentrations. The most intense peak in the spectrum, called the base peak is assigned a value of 100% and the intensities of the other peaks, including the molecular ion peak, are reported as percentages of the base peak. Sometimes the molecular peak may be the base peak.

2.2.4. Types of Ionization:

There are four types of Ionization methods.

- 1. Electron Impact mode
- 2. Chemical ionization method
- Field disorption
- 4. Fast atom bombardment
- 1. Electron Impact Mode: In this method a mass spectrometer bombards molecules in the vapour phase with a high energy electron beam and records the result of electron impact as a spectrum of positive ions separated on the bases of mass I charge (m/z)

Sufficiently stable molecular ion cannot be formed by this method. This is because of large amount of excess energy imparted to the molecular ion by 70ev bombardment.

Base peak: A mass spectrum is a presentation of the masses of the positively charged fragments versus their relative concentrations. The largest peak in the spectrum, called the base peak. It's intensity is taken as 100% and the intensities of other peaks, including the molecular ion peak, are reported as percentages of the base peak. The molecular ion peak may sometimes be the base peak. In the below example molecular ion peak is m/z '121', and base peak is m/z 77.

Eg

2.2.5. Fragmentation of Organic Compounds :

Cleavage is favoured at alkyl substituted carbon atoms, the more substituted, the more likely is cleavage. This is a consequence of the increased stability of a tertiary carbocation over a secondary, which in turn is more stable than a primary. Generally, the largest substituent at a branch is eliminated most readily as a radical, because a long – chain radical can achieve some stability by delocalization of the lone electron.

II σ Bond rupture near functional groups: This is facilitated by the easier ionization of non bonding orbitals of hetero atom than the σ bonding orbitals. The C-C bond next to a hetero atom are frequently cleaved, leaving the charge on the fragment containing the hetero atom whose non bonding electrons provide resonance stabilization.

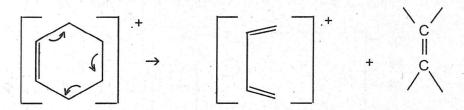
$$CH_3 - CH_2 - Y - R \xrightarrow{-CH_3} CH_2 = Y^+ - R \leftrightarrow CH_2 - Y - R$$

Y=O, NH, or S.

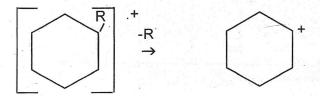
III Double bonds favour allylic cleavage and the resonance stabilized allylic carbocation. This rule does not hold for simple alkenes because of the ready migration of the double bond, but it does hold for cycloalkenes.

$$CH_2$$
⁺: $CH - CH_2 - R \xrightarrow{-R} + CH_2 - CH = CH_2 \leftrightarrow CH_2 = CH_2 + CH_2$

IV Elimination by multiple σ bond rupture: Elimination by multiple σ -bond rupture may occur, leading to the extrusion of a neutral molecule such as CO, C_2H_4 , C_2H_2 , etc.. A well known example is the Retro -Diels - Alder reaction of cyclo hexenes.



V) Saturated rings tend to lose: Alkyl side chains at the ' α ' bond. This is merely a special case of branching. The positive charge tends to stay with the ring fragment.



VI) In alkyl – substituted aromatic compounds, cleavage is very probable at the bond β to the ring giving the resonance - stabilized benzyl ion or, more likely, the tropylium ion.

226

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VI) Even Electron Rule: This is based on thermodynamic principles. It states that an even electron species will not normally fragment to two odd electron species i.e., an ion will not fragment to a radical and a radical ion since the total energy of this product mixture will be too high.

$$A^+ \longrightarrow B^+ + C$$

In Preference, an ion will degrade to another ion and a neutral molecule.

$$A^+ \longrightarrow B^+ + C$$
 even even

Radical ions, being odd – electron species, can extrude a neutral molecule, leaving a radical ion as co product.

$$A^+ \longrightarrow B^+ + C$$
Odd ever

Radical ions can also degrade to a radical and an ion

VII) Some times cleavage is often associated with rearrangement.

Eg. Mc Lafferty rearrangement in carbonyl compounds

2.2.6. Meta Stable Peak: Meta stable peaks can be easily determined in a mass spectrum.

Some important characteristics of these peaks are:

- i) They do not necessarily occur at the integral m/e. values
- ii) These are much broader than the normal peaks and
- iii) These are of relatively low abundance.

Formation of meta stable ions: consider that M_1^+ is the parent ion and m_1^+ is the daughter ion. If the reaction $M_1^+ \to m_1^+$ takes place in the source, then the daughter ion, m_1^+ may travel the whole analyzer region and is recorded as m_1^+ ion. On the other hand, if the transition M_1^+ to m_1^+ occurs after the source exist and before arrival at the collector, then m_1^+ is called a meta stable ion. The peak for m_1^+ will not appear at the normal position for m_1^+ on the mass scale. Instead the signal appears at m_1^2/M_1 . Hence we conclude that the position of meta stable peak (m^*)due to the reaction $M_1^+ \to m_1^+$ is such that

$$m *= m_1^2 / M_1$$

It is important to remember that for a reaction $M_1^+ \to m_1^+, m^*$ (meta stable peak) has a distance blow m, on the mass scale. The distance is approximately similar to the distance that m, lies below M,.

2.2.7. Mc Lafferty Rearrangement:

It involves the migration of γ -hydrogen atom followed by the cleavage of a β – bond. The rearrangement leads to the elimination of neutral molecules from aldehydes, ketones, amines, unsaturated compounds, substituted aromatic compounds etc. The rearrangement proceeds through a sterically hindered six membered transition state ex: Ketone.

Ex: Butanal

Molecular ion

Thus the molecular formula of the unknown compound can be determined from the various fragment ions and also the parent ion of mass spectrum.

n-Propyl benzene shows a Mc Lafferty rearrangement ion peak in large abundance at m/e 92.

A double Mc Lafferty rearrangement is also reported in certain ketones. The second hydrogen atom originates exclusively from the γ -position. The mechanism involves.

- i) Ketonisation of the intermediate enol ion by the hydrogen transfer
- ii) Hydrogen transfer to enolic oxygen.

Ex: 4 - Heptanone

$$H_2C$$
 H_2C
 CH_2 - CH_2 - CH_2 CH_3
 H_2C
 CH_2 - CH_2 - CH_3
 H_2C
 CH_2 - CH_3
 H_2C
 CH_2 - CH_3
 H_2C
 CH_2 - CH_3
 H_2C
 CH_2 - CH_3
 CH_2 - CH_3
 CH_3 - CH_3
 CH_4 - CH_4 - CH_5
 CH_5 - CH_5
 CH_5 - CH_5 - CH_5
 CH_5 - CH_5 -

2.2.8. The Nitrogen Rule: It states that 'a molecule of even numbered molecular mass must contain no nitrogen atom or an even number of nitrogen atoms. An odd numbered molecular mass requires an odd number of nitrogen atoms'.

This rules for all compounds containing carbon, Hydrogen, Oxygen, Nitrogen, Sulphur and halogens.

An important rule states that the fragmentation at a single bond gives an odd numbered ion fragment from an even numbered molecular ion. Similarly an even numbered ion fragment results from an odd numbered molecular ion. For this corollary to hold, the fragment ion must contain all the nitrogen atoms of molecular ion.

Let us consider Nitro benzene ($C_6H_5No_2$). The signal for molecular ion appears at m/e 123, i.e. at odd numbered molecular mass since the compound contains only one nitrogen atom. Two important ion fragments which are formed in the small spectrum of this compound are i) NO_2^+ at m/e 4b and ii) NO^+ at m/e 30. Both these appear at even mass number.

Consider 2, 4 dinitro phenol containing even number (2) of the nitrogen atoms. Its molecular ion signal appears at m/e 184. The fragment ions appear at I) (M⁺-H) i.e., at m/e 183 and ii) (M⁺-H-CO) at m/e 155. Thus we see that fragments containing both the nitrogen atoms appears at odd mass number. This proves the validity of the Nitrogen rule.

There are two important categories of magnetic deflection mass spectrometers. Low resolution & High resolution.

Low resolution instruments can be defined arbitrarily as instruments that separate unit masses upto m/e 2000. [R- 2000 / 2000 - 1999) = 2000]

As instrument is generally considered high resolution if it can separate two ions differing in mass by at least one part in ten thousand to fifteen thousand (R = 10,000 - 15,000). An instrument with 10,000 resolution can separate an ion of mass 500.00 from one of mass 499.95 (R = 500 / 0.05 = 10,000). This important class of mass spectrometers can measure the mass of an ion with sufficient accuracy to determine its atomic composition.

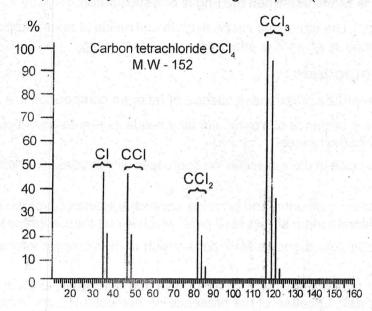
Aliphatic chlorides: The molecular ion peak is detectable only in the lower monochlorides. Fragmentation of the molecular ion is mediated by Cl atom but to a much lesser degree than is the case in –O, -N, or –S containing Compounds. Thus cleavage of straight chain monochloride at the C-C bond adjacent to Cl atom accounts for a small peak at m/e 49.

$$\overrightarrow{R-CH_2-Cl:} \rightarrow \overrightarrow{CH_2} = \overrightarrow{Cl:} \leftrightarrow \overrightarrow{CH_2-Cl:}$$

Cleavage of the C-Cl bond leads to a small Cl $^+$ peak and to a R $^+$ peak which is prominent in lower chlorides but quite small when the chain is longer than about C $_5$.

Straight chain chlorides longer than C_6 give $C_3H_6Cl^+, C_4H_8Cl^+, C_5H_{10}Cl^+$ ions. Of these $C_4H_8Cl^+$ ion forms the most intense (sometime the base) peak. A five membered cyclic structure explains its stability.

Loss of HCl Occurs, possibly by 1,3 elimination to give a peak (Weak or moderate) at M-36



Aliphatic Bromides: The remarks under aliphatic chlorides apply to corresponding Bromides.

Aliphatic lodides : They give the strongest molecular ion peak of aliphatic halides. Since I_2 is mono isotopic, there is no distinctive isotope peak.

lodides cleave much as do chlorides & bromides but $C_4 H_8 I^+$ ion is not as ϵ dent as the corresponding chlorides and bromide ions.

Aliphatic Fluorides: They give the weakest molecular ion peaks of the aliphatic handless. Fluorine is monoisotopic and its detection in polyfluoro compounds depends on suspicious small isotopic peaks relative to molecular ion, on the intervals between peaks and on characteristic peaks.

Of these the most characteristic is m/e 69 due to ion CF_3^+ which is the base peak in all perfluoro carbons. Prominent peaks are noted at m/e 119, 169, 219..... these are increments of CF_2 . The stable ions $C_3F_5^+$ & $C_4F_7^+$ give large peaks at m/e 131 and 181. In mono fluorides cleavage of the $\alpha\beta$ C-C bond is less important than in other monohalides but cleavage of a C-H bond on the α -C is more important. This reversal is a consequence of high E N of F atom and is rationalized by placing +ve charge on α carbon. The secondary carbonium ion thus depicted by a loss of a H atom is more stable than the I^o carbonium ion resulting from loss of an alkyl radical.

$$\begin{bmatrix} R - CH_2 - F \end{bmatrix}^+ \xrightarrow{-H} R - CH - F$$

$$-R \xrightarrow{+} CH_2 - F$$

Benzyl Halides: The molecular ion peak of benzyl halides is usually detectable. The benzyl (or tropylium) ion from loss of the halide is favoured even over β bond cleavage of an alkyl substituent. A substituted phenyl ion is prominent when the ring is polysubstituted

Aromatic Halides: The molecular ion peak of an aryl halide is readily apparent. The M-X peak is large for all compounds in which X is attached directly to the ring.

2.2.9. Halogen Compounds:

Some important features of the mass spectra of halogen compounds are :

- a) The molecular ion abundance of a particular alkyl halide increases as the electronegativity of the halogen substituent decreases.
- b) The relative abundance of the molecular ion decreases with increase in chain length and increase in branching.
- c) Compounds containing chlorine and bromine show characteristic isotope peaks. A compound containing one chlorine atom shows M+2 peak which is one third in intensity of parent ion peak.
- d) A mono bromo compound shows M+2 peak which is of the same intensity compared to the parent peak.
- e) A compound that contains 2 Cl or 2 Br or one Cl and one Br will show a distinct M+4 peak in addition to M+2 peak, because of the presence of molecular ion containing 2 atoms of heavy isotopes.
- f) In the parent ion, charge resides on the halogen atom.
- g) Important fragmentation mode is α cleavage with charge retention by halogen containing fragment. Another mode leads to loss of halide radical.

$$R - CH_2 - X \rightarrow CH_2 = X + R$$

$$R - CH_2 - X \rightarrow RCH_2 + X (Preferable mode)$$

Molecular Ion: A molecular ion is produced when a neutral molecule loses an electron. This 'e' is lost from the highest molecular orbitals of organic compounds. A molecular ion should not be represented by a localized structure unless there is a specific evidence.

Molecular Ion Peak: The ion cluster appearing at highest 'm/z' value represents the molecular ion with its attendent 'M+1'. peaks etc. Molecular ion peak may be weak or it may not appear at all. The intensity of the molecular ion peak depends on the stability of molecular ion. The most stable molecular ions are produced from purely aromatic systems. If substituents that have favourable modes of cleavage are present the molecular ion peak will be less intense and the fragment peaks

relatively more intense. In general, the following group of compounds will be in the order of decreasing ability, give prominent molecular ion peaks.

Aromatic compounds > conjugated alkenes > cyclic compounds > organic sulfides > Short, normal alkanes > mercaptans Recognizable molecular ions are usually produced for these compound in order of decreasing ability.

Ketones > amines > esters > ethers > carboxylic acids ~ aldehydes ~ amides ~ halides.

The presence of an M-15 peak (loss of CH_3) or an M-18 peak (loss of H_2 O or an M-31 peak (loss of OCH_3 from methyl esters) and so on, it is taken as confirmation of a molecular ion peak. An M-1 peak is common, and occasionally an M-2 peak (loss of H_2 by either fragmentation or thermolysis), or even a rare M-3 peak is reasonable.

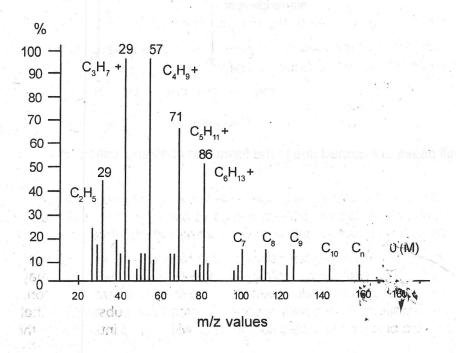
Loss of 16(O), 17(OH), or 18 (H₂O) are likely only if an oxygen atom is in the molecule.

The intensity of a molecular ion peak is comparitively greatest for straight chain compounds than branched compounds. The intensity of molecular ion peak decreases with increasing molecular weight in a homologous series except fatty acids.

2.2.10. Alkanes: The molecular ion will normally be seen in the mass spectra of the lower nalkanes. But its intensity falls off with increased size and branching of the chain.

Eg: Dodecane

The fragmentation pattern is characterized by Clusters of peaks, and corresponding peaks of each cluster are 14 ($\mathrm{CH_2}$) mass units apart. The largest peak in each cluster represents a $\mathrm{C_nH_{2n+1}}$ fragment and this occurs at m/z = 14 n+1, this is accompanied by $\mathrm{C_nH_{2n}}$ and $\mathrm{C_nH_{2n-1}}$ fragments. The most abundant peaks are produced by $\mathrm{C_3H_7^+}$ and $\mathrm{C_4H_9^+}$



Branched Chain Alkanes: Some important features of the mass spectra of branched chain alkanes are:

Bond cleavage takes place preferably at the site of branching due to such cleavage, a more stable secondary or tertiary carbonium ion results.

Generally, largest substituent at a branch is eliminated readily as a radical. The radical achieves stability by delocalisation of lone electron

Molecular ion is not formed

Great number of fragments results from a branched chain compound compared to the straight chain compound. It is due to greater pathways available for cleavage:

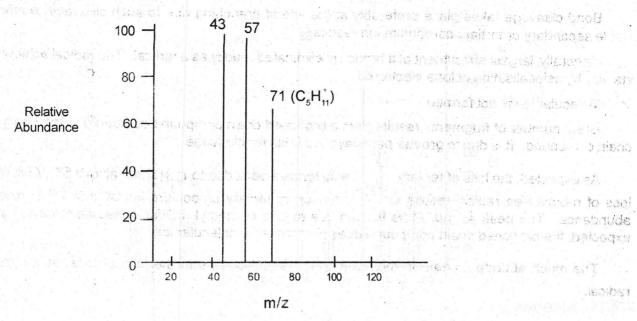
As expected, the loss of tertiary discal forms a peak due to $C_4H_9^+$ ion at 'm/z 57'. Also the loss of n-butyl free radical results in mation of tertiary carbonium ion at 'm/z 71' in much abundance. The peak at 'm/z 71' is formed due to loss of methyl radical in less abundance. As expected, the branched chain compound does not form any molecular ion.

The much abundant peak at 'm/z 43' $(C_3H_7^+)$ is formed due to the loss of most stable free radical.

CH₃ CH₂ - CH₂ - CH₂ - CH₂ - CH₂ - CH₃
$$\rightarrow$$
 CH₃ - CH₂ + CH₃ - CH-CH₂

CH₃ CH₃ CH₃ \rightarrow CH

Also small peaks are formed due to the formation of alkenyl cation.



Cyclo Alkanes:

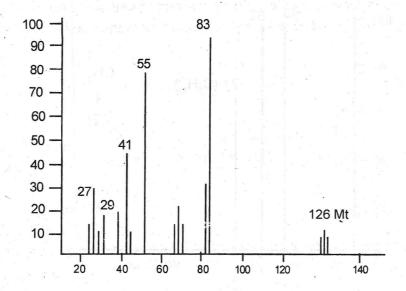
The relative abundance of the molecular ion of cyclo alkane is more as compared to the corresponding alkane.

It favours cleavage at the bond connecting the ring to the rest of the molecule.

Fragmentation of the ring is usually characterized by the loss of two carbon atoms as ${
m C_2H_4}(28)$ and ${
m C_2H_5}^+(29)$

The stability of the fragment ion depends upon the size of the ring.

- a) The peak m/e 128, is the molecular ion peak and is quite abundant.
- b) The largest peak (base peak) at 'm/z 83' is formed by the loss of the side chain. The lone electron remains on the ring. This positively charged ion radical appears at m/z 83
- c) The ion radical shows Retro Diel's Alder reaction and fragment ion is formed at 'm/z 55'. The abundance of this ion is very large.



2.2.11. Alkenes:

a) The molecular ion peak in the spectra of unsaturated compound is more intense than the corresponding saturated analogues. The reason is the better resonance stabilization of the charge on the cation formed by the removal of one of $\pi-$ electrons. Mono olefins contain $C_nH^+_{2n-1}$ ions in their mass spectra.

The relative abundance of the molecular ion peak decreases with increasing molecular mass.

A cyclic olefin also shows group of peaks which are 14 mass units apart.

The general mode of fragmentation induced by a double bond is the allylic cleavage.

The C_nH_{2n} ions formed by Mc Lafferty rearrangement are more intense. For example, Mc Lafferty rearrangement ion is formed at m/e 42 from 1-pentene due to loss of ethylene molecule.

H₂C
$$CH_2$$
 CH_2 C

Cyclic olefins usually show a distinct molecular ion peak. They undergo Retro – Diels – Alder reaction.

2.2.12. Alkyl Aromatic Compounds:

- 1. The molecular ion peak in aromatic compounds is fairly abundant as compared to the corresponding alkanes and alkenes containing the same number of carbon atoms.
- 2. In aromatic compounds $M^+ + 1$ and $M^+ + 2$ are also noticed. The reason is fairly large abundance of the molecular ion peak.
- 3. In case of polynuclear hydrocarbons, doubly or triply charged ions $(M^{2+}, M^{3+} ions)$ are possibly formed. Doubly charged molecular ions (m/z) appear at integral 'm/z' values.
- 4. If the aromatic ring is substituted by an alkyl group, a prominent peak is formed at m/e 91. Here benzyl $(C_6H_5^+CH_2)$ cation formed rearrangements to tropylium cation $(C_7H_7^+)$. The fragmentation pattern of n-propyl benzene is shown below.

$$(M^{+}) \text{ m/z - 120}$$

$$CH_{2}\text{-CH}_{2}\text{-CH}_{3}$$

$$-(CH_{3}\text{- CH}_{2})$$

$$Benzyl Cation$$

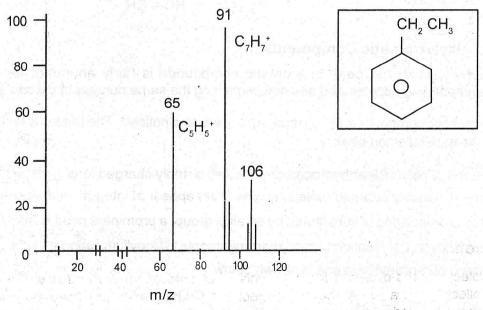
$$M^{+} \sum_{m/z} \frac{Loss \text{ of } -(CH \equiv CH)}{(CH \equiv CH)}$$

The benzyl cation formed rearranges to more stable tropylium cation which appears at 'm/e 91'. Tropylium cation in turn loses a molecule of acetylene to form $C_5 \, \mathrm{H_5^+}$ at m/e 65.

5. Hydrogen migration with elimination of neutral alkene molecule accounts for the peak at m/z 92 observed when the alkyl group as longer than ${}^{\circ}C_2{}^{\circ}$.

A characteristic cluster of ions due to a α cleavage and hydrogen migration in mono alkyl benzenes appears at m/z 77 $\left(C_6H_6^+\right)$ 78 $\left(C_6H_6^+\right)$ and 79 $\left(C_6H_7^+\right)$.

The mass spectrum of ethyl benzene is shown below



2.2.13. Ethers:

- 1. Electron bombardment dislodges a non-bonding electron from oxygen.
- 2. Fragmentation of the resulting molecular ion occurs in two principal ways.
- a) A carbon oxygen bond is cleaved heterolytically with the electron going to the more electronegative oxygen atom.

CH₃ CH₃
$$\downarrow$$
 CH₃ CH₃ \downarrow CH₃ CH₃ \downarrow CH₃ CH₂ CH OCH₃ \downarrow CH₃ CH₃ \downarrow CH₃ CH₃ CH₃ CH₃ CH₃ CH₃ \downarrow CH₃ CH₃

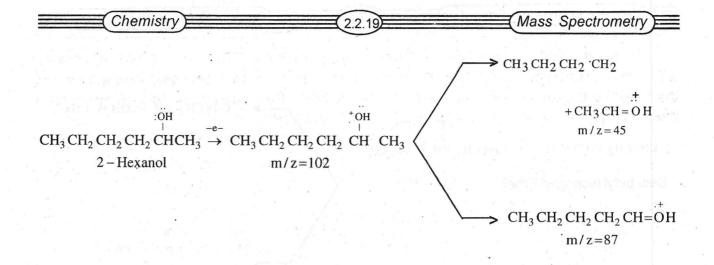
 $\left[\mathrm{C_{3}H_{7}^{+}} \right]$ (m/z = 43) is the molecular ion peak

b) A carbon – carbon bond is cleaved homolytically at the α –position because it leads to a square resonance - stabilized cation. The largest α - substituent is the one most readily cleaved.

2.2.14. Alcohols:

The molecular ions obtained from alcohols fragments so readily that few of them survive to reach the collector. As a result, the mass spectra of primary and secondary alcohols show weak molecular ion peaks, and the molecular ions from 3° alcohols are not detectable.

Alcohols, like alkyl halides and ethers undergo α - cleavage, with the largest α -substituent being the one most readily cleaved. Consequently, the mass spectrum of 2-hexanol shows a base peak at m/z - 45 (α -cleavage of a butyl radical) and a smaller peak at m/z = 87 (α -cleavage of a methyl radical)



Alcohols show a peak m/z = m-18 due to loss of water that is eliminated comes from the 'OH' group of alcohol and γ – hydrogen.

CH₃ CH₂ CH CH₂ CH CH₃
$$\rightarrow$$
 CH₃ CH₂ CH CH₂ CH CH₃ + H₂O
$$\frac{H}{CH_3} \stackrel{+}{CH} \stackrel{+}{CH} \stackrel{-}{CH} \stackrel{-}{CH$$

- 1. A bond between carbon and a more electronegative atom breaks heterolytically.
- 2. A bond between carbon and an atom of similar electronegativity (a carbon or a hydrogen) breaks homolytically.
- 3. The bond most likely to break are those that lead to the most stable cation.
- **2.4.15. Ketones**: The mass spectrum of ketones generally has an intense molecular ion peak. Ketones fragment homolytically at the carbon carbon bond adjacent to the carbon oxygen double bond (α -cleavage) which results in the formation of a resonance stabilized cation. The larger alkyl group is the one most easily cleaved.

If one of the alkyl groups attached to the carbonyl carbon has a γ -hydrogen, a cleavage known as a 'Mc Lafferty rearrangement' may occur. In this rearrangement the bond between the α - carbon and the β - carbon breaks homolytically and a hydrogen atom from the oxygen atom. Again, fragmentation has occurred in a way the produces a resonance stabilized cation.

H₂C
$$\xrightarrow{H_2}$$
C $\xrightarrow{H_2}$ C

2.2.16. Suggested Readings

- 1. Some Modern methods of Organic Synthesis, W. Carruthers, Cambridge University Press.
- 2. Advanced Organic Chemistry, Reactions Mechanisms and Structure,
 J. March. John Wiley
- 3. Advanced Organic Chemistry Part B, F.A. Carey and R.J. Sundberg, Plenum Press 1.
- 4. Spectrometric Identification of Organic Compounds, R. M. Silverstein, G.C. Bassler and T. C. Morrill, John Wiley.
- 5. Applications of Spectroscopy of Organic Compounds, J. R. Dyer, Prenctice Hall.
- 6. Spectroscopic methods in Organic Chemistry, D.H. Williams, I. Fleming, Tata Mc. Graw Hill
- 7. Spectroscopic methods in Organic Chemistry Kemp
- 8. Fundamentals of Photochemistry, K.K. Rohtagi Mukherji, Wiley Eastern
- 9. Text Book of Organic Chemistry Vol I & II I. L. Finar.